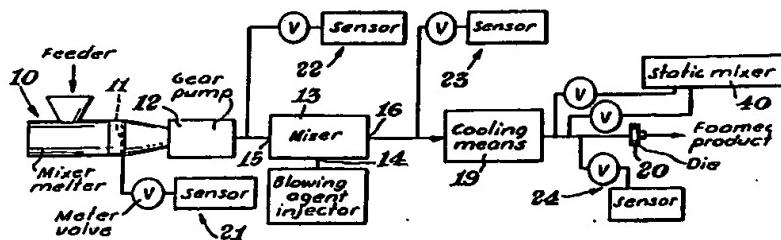




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :  B29B 7/30, 7/32, 7/46 C08J 9/12, 9/14, 9/30		A1	(11) International Publication Number: WO 90/07407  (43) International Publication Date: 12 July 1990 (12.07.90)
(21) International Application Number: PCT/US89/05865  (22) International Filing Date: 22 December 1989 (22.12.89)  (30) Priority data: 290,598 27 December 1988 (27.12.88) US		(81) Designated States: BR, FI, NO.  Published <i>With international search report.</i>	
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(54) Title: METHOD AND APPARATUS FOR PREPARING THERMOPLASTIC FOAM



## (57) Abstract

Thermoplastic foam is prepared by a continuous process comprising melt mixing thermoplastic resin (10); pressurizing the resin melt (12); introducing blowing agent (14); cooling and depressurizing the resultant gel (19); and either foaming and forming the gel to form a foamable composition (20). The process temperature is maintained substantially independently of the flow rate of the resin melt and gel at below that at which substantial degradation of the resin gel occurs. The process has particular application to rubber-modified polystyrene or rubber-modified polyethylene resin foam compositions containing a fire retardant.

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-1-

METHOD AND APPARATUS FOR PREPARING  
THERMOPLASTIC FOAM

The present invention relates generally to a method and an apparatus especially useful for low temperature preparation of thermoplastic foam compositions. The present invention also relates to 5 novel foam compositions containing highly desirable amounts of rubber and fire retardant.

Commercial preparation of thermoplastic foam composition was disclosed in the 1930's. An early 10 disclosure, Munter et al., U.S. Patent No. 2,023,204, teaches a batch process for preparation of foam boards wherein thermoplastic resin is melted in a pressurized vessel containing a blowing agent. A valve opening in the vessel allows the resin to foam directly into the 15 outside air or into a shaping vessel.

With the advent of continuous foam processing utilizing extruder apparatuses, an improved foam product was made possible at lower cost thus resulting in 20 widespread commercial use. Numerous processes were developed in efforts to improve the extruder apparatus and hence improve methods of preparation.

-2-

McIntire, U.S. Patent No. 2,515,250 discloses a continuous process for making thermoplastic foam compositions and an apparatus for preparing foam compositions which includes a separate  
5 temperature/pressure regulating zone located between an extruder and a pressurized storage vessel.

Winstead, U.S. Patent No. 3,830,901 discloses a continuous process for extruding thermoplastic foam  
10 compositions and an apparatus consisting of an extruder, a gear pump, a cooling zone and a die.

Presently, commercial production of thermo-plastic foam typically utilizes an apparatus in which an  
15 extruder is a means for melting and pressurizing a resin to a resin melt, and mixing additives and blowing agents with the melt to form a resin gel. Subsequently the gel is forwarded through a cooling-depressurizing means and a foaming means.  
20

The production of thermoplastic resin foam must necessarily be carried out above the glass transition temperature (Tg) or the melt temperature (Tm) of the resin. Above the Tg or Tm there exists an optimum  
25 temperature range for producing foam compositions possessing good structural integrity. Among the parameters which determine the optimum operational temperature are the weight average molecular weight (MW)  
30 distribution of the resin and the nature and amount of the additives in the resin gel. For example, the optimally desirable temperature range for processing a polystyrene resin gel of weight average MW of approximately 200,000 having a glass transition  
35 temperature of about 100°C (degrees centigrade) is in the range of about 140°C to about 195°C. Other

-3-

temperature ranges apply to other resins and other resin/additive combinations.

In commonly used commercial processes for production of foam compositions at optimum production rates, the resin gel temperature ranges exceed optimum temperature ranges. For example, the temperature range for processing polystyrene gel usually ranges from about 200°C to about 250°C. The higher temperatures above 200°C occur when output rates exceed about 200 lbs/hr (90 kg/hr). The high gel temperatures at high production rates are attributed to thermal energy generated by shear forces created by extruder screw movement. Gel temperatures in excess of that required for melting the resin cause certain problems.

One problem arises when a fire retardant is introduced into the resin melt. At temperatures above about 190°C, commonly used halogenated fire retardants such as hexabromocyclododecane (HBCD), pentabromomonochlorocyclohexane (PBCH) and tetrabromobisphenol A (TBBA) exhibit sufficient degradation resulting in a significant amount of free radical degradation product. The free radicals react with the polymeric backbone of the resin gel resulting in chain scissions which reduce the weight average molecular weight (MW) of the resin. A lower MW resin undesirably effects the structural properties of the resultant foam composition.

One technique commonly employed to compensate for MW loss, is to initiate the foam-making process with a resin of higher average MW than the desired MW of the resultant foam composition. However, the use of higher MW resin does not completely solve temperature related degradation problems. As the MW of the resin increases,

-4-

the viscosity of resin gel increases causing an increase in the shear forces in the extruder mixing chamber. In turn, increased shear forces create an increase in the resin gel temperature causing a further degradation in  
5 additives and resin.

A further drawback to high temperature processing concerns limitations on the types of foam compositions which can be produced. For example, foam  
10 compositions containing a high rubber content and also containing a desirably high content of a preferred fire retardant are not easily produced at high temperatures. The rubber phase of the resin gel degrades readily and  
15 halogenated fire retardants enhance the degradation process.

Because of the above-listed limitations and problems imposed on the preparation of foam using an extruder it would be highly desirable to find an  
20 alternative method for preparing certain thermoplastic foam compositions.

The present invention provides a solution to the problems encountered in the preparation of  
25 thermoplastic resin foam at high throughput rates which cause undesirably high temperature ranges. Improved rubber-modified foam compositions can be produced at lower temperatures without sacrificing throughput rates  
30 by utilizing the apparatus and method of the present invention.

Briefly there are three major aspects to the invention. In one aspect, the present invention relates  
35 to novel foam products. For example, the novel foam product can be a thermoplastic resin foam composition

-5-

comprising a rubber-modified polyethylene resin or a rubber-modified polystyrene resin and 0.01 weight percent to 5 weight percent by resin weight of a fire retardant wherein the rubber-modified resin has  
5 dispersed rubber particles in a polymeric matrix in an amount of 3 weight percent to 30 weight percent of the total resin weight. Other aspects of the invention relate to a method and an apparatus for continuous preparation of thermoplastic foam compositions; which  
10 method and apparatus demonstrate improved energy-efficient preparation of foam at low temperature ranges wherein the resin melt and resin gel temperatures are maintained essentially independently of the throughput rate. Thus, low temperature processing of foams is  
15 provided at high output rates.

In another aspect the present invention comprises a continuous method for preparation of a  
20 thermoplastic resin foam or foamable composition sequentially comprising the steps of:

(a) melting and mixing at least one thermoplastic resin to form a resin melt, the mixing process being carried out without applying shear forces of sufficient thermal energy to cause a localized rise in temperature to a temperature at which substantial degradation of the resin melt occurs;

(b) pressurizing to and maintaining the resin melt at a pressure sufficient to permit introduction of one or more blowing agents into the resin melt at a temperature below the temperature at which substantial degradation of the resin melt occurs;

35

-6-

(c) introducing and dispersing one or more blowing agents substantially throughout the resin melt to form a resin gel at a temperature above the glass transition temperature or the melt temperature of the 5 thermoplastic resin and below a temperature at which substantial degradation of the resin gel occurs; and

(d) cooling and depressurizing the resin gel, the depressurizing being carried out at a sufficiently 10 cool temperature for formation of a foam composition with structural integrity, and the cooling and depressurizing being carried out substantially at the same time;

15 (e) either foaming and forming the resin gel to form a solid foam composition or foaming the resin gel to form a solid foamable composition;

the recited steps being carried out  
20 continuously in a series of stages with the temperature of the resin melt and gel being maintained substantially independently of the flow rate of the resin melt and gel advancing through and between the stages.

25 The method for preparation of thermoplastic resin foam compositions of the present invention provides an alternative to presently-used extrusion methods and a considerable improvement over batch methods. Optimum production rates can be maintained 30 while allowing processing at lower gel temperatures.

In a still further aspect the present invention relates to an apparatus for continuous production of thermoplastic resin foam or foamable compositions by the 35 method of this invention, said apparatus comprising:

-7-

- (a) melting-mixing means for melting and mixing at least one thermoplastic resin to form a resin melt, the melting-mixing means having moving mixing elements and being adapted by the spacing between the 5 moving mixing elements and interaction thereof to accomplish substantial mixing of the resin melt essentially without shear forces of sufficient thermal energy to cause a localized rise in the temperature of the resin melt to greater than 150°C above the glass 10 transition temperature or melt temperature of the resin; the melting-mixing means having an inlet for the resin and an outlet for the resin melt, and means for causing the resin melt to discharge from the outlet;
- 15 (b) pump means for pressurizing the resin melt to a pressure in the range of 1000 pounds per square inch gauge (psig) (7000 kiloPascals gauge (kPag)) to 10,000 psig (70,000 kPag), the pump means having an inlet and an outlet and means for metering the resin 20 melt through the outlet;
- 25 (c) pressurized mixing means for dispersing one or more blowing agents into the resin melt within a pressurized zone to form a resin gel, the pressurized mixing means being provided with an inlet for introducing the blowing agents, an inlet for the resin melt, and an outlet for discharging the resin gel under pressure;
- 30 (d) cooling-depressurizing means for concurrently cooling the resin gel within a pressurized zone and discharging the resin gel through a foam-forming die orifice means to form a solid foam 35 composition; the cooling-depressurizing means having an

-8-

inlet for receiving the resin gel under pressure and an outlet for the cooled gel; and

- (e) conduit means providing fluid communication respectively and sequentially between the outlet of the melting-mixing means and the inlet of the pump means, between the outlet of the pump means and the inlet of the pressurized mixing means, between the outlet of the pressurized mixing means and the inlet of the cooling-depressurizing means and between the outlet of the cooling-depressurizing means and the foam-forming die orifice means.

Referring to the drawings, Fig. 1 is a schematic diagram illustrating an embodiment of the apparatus of the present invention. This combination of equipment means produces continuously extruded thermoplastic foam compositions as further explained in Example 1;

20

Fig. 2 is a schematic diagram illustrating another embodiment of the apparatus of the present invention in which the means for pressurized mixing of blowing agents in the resin melt has been modified to comprise a combination of two modes for pressurized mixing means as further explained in Example 3.

One embodiment of the invention comprises novel rubber-modified polystyrene resin foam compositions and rubber-modified polyethylene resin foam compositions having about 0.01 weight percent to about 5 weight percent by resin weight of a fire retardant, preferably about 1 weight percent to about 3 weight percent, with the balance of the foam composition being rubber-modified polystyrene resin or rubber-modified

-9-

polyethylene resin and any other additives, including blowing agents. The resin has dispersed rubber, preferably polymeric butadiene particles in a polymeric matrix in an amount of about 3 weight percent to about 5 30 weight percent of the resin weight, preferably about 3 weight percent to about 22 weight percent, more preferably about 3 weight percent to about 16 weight percent. The fire retardant preferably is a halogenated compound from the group consisting of HBCD, 10 PBCH and TBBA. The blowing agents and additives described in this specification are used in amounts that are well-known in the art.

15 The foam composition is essentially a closed cell rigid foam with a density ranging from at least about 1 pound per cubic foot ( $lb/ft^3$ ) (16 kilograms per cubic meter ( $kg/m^3$ )) to about 10  $lb/ft^3$  (160  $kg/m^3$ ), preferably about 1.0  $lb/ft^3$  (16  $kg/m^3$ ) to about 20 5.0  $lb/ft^3$  (80  $kg/m^3$ ), more preferably about 1.0  $lb/ft^3$  (16  $kg/m^3$ ) to about 2.5  $lb/ft^2$  (40  $kg/m^3$ ). The cell diameter ranges from about 0.1 mm (millimeter) to about 4 mm, preferably from about 0.2 mm to about 2.5 mm, more preferably from about 0.2 mm to about 1 mm.

25 Among the thermoplastic resins which can be utilized to produce corresponding foam compositions using the apparatus and method of the present invention are polymers such as styrenic polymers disclosed in Suh, 30 U.S. Patent No. 4,085,073. Other olefinic polymers and copolymers can be foamed using this process such as polyethylene, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultra low density polyethylene, copolymers of ethylene/vinyl acetate, high 35 density polyethylene (HDPE), copolymers of ethylene/acrylic acid (EAA), polypropylene (PP),

-10-

polyesters, polycarbonates rubber modified polystyrenes, acrylonitrile-butadiene-polystyrene (ABS), polyvinyl chloride (PVC), polyvinylidene copolymers, high bromine containing rubber modified polystyrene, ethylenic ionomers, styrenic ionomers and mixtures thereof.

Among the blowing agents which can be used are halocarbons and halo hydrocarbons such as chlorofluorocarbons and fluorocarbons, chlorofluorohydrocarbons and fluorohydrocarbons, water, carbon dioxide, halogenated lower alkyls such as methyl and ethyl chloride, lower alkyls containing one to about 6 carbon atoms such as butane, nitrogen gas, and oxygen gas. Preferred blowing agents comprise the halo hydrocarbons such as fluorohydrocarbons or chlorofluorohydrocarbons containing at least one hydrogen atom attached to a carbon atom, water, carbon dioxide, methyl chloride and ethyl chloride and mixtures thereof.

Additives which may be mixed with the thermoplastic resin to make a thermoplastic resin melt include fire retardants, cell nucleating agents, cell enlarging agents, plasticizers, acid scavengers, colorants, antioxidants, lubricants, antistatic agents and corrosion inhibitors among others.

Among the fire retardants which can be used and are preferred are bromine containing cycloalkyls, most preferably HBCD, PBCH, and TBBA.

Cell nucleating agents include but are not limited to talc, indigo, phthalocyanine blue, magnesium oxide and metal stearates. Preferred cell nucleating agents include talc, indigo, magnesium oxide and metal

- 11 -

stearates. The more preferred cell nucleating agent is talc.

5 Among the cell enlarging agents are waxy materials, LDPE, and LLDPE. Preferred cell enlarging agents comprise LDPE and LLDPE.

10 Among the plasticizers are saturated aliphatic oils containing about 1 to about 22 carbon atoms. Preferred plasticizers are diacetyl phthalate, dihexyl phthalate, and saturated aliphatic oils such as mineral oil.

15 Acid scavengers include but are not limited to magnesium oxide and tetrasodiumpyrophosphate (TSPP).

20 A novel aspect of the invention is that the melting-mixing and pressurizing of the resin melt and any dispersion therein of blowing agents to form a thermoplastic foam product are each carried out as 25 individually controlled steps thereby permitting the gel temperature to be controlled essentially independently of the throughput rate without raising the resin temperature by the work put into it. Thus, low temperature continuous preparation of thermoplastic resin foam compositions at advantageous throughput rates is enhanced and assured.

30 In steps (a) through (c) of the above-mentioned method of the present invention, the temperature of the resin gel can range from about 40°C to about 150°C above the glass transition temperature (Tg) or melt temperature (Tm) of the resin, preferably from about 40°C to about 100°C above the Tg or Tm and more

35

-12-

preferably from about 50°C to about 90°C above the T<sub>g</sub> or T<sub>m</sub>.

The melting-mixing step (a) preferably includes  
5 pre-pressurizing of the resin melt to a pressure in the range from about 0.01 psig (0.07 kPag) to about 980 psig (6800 kPag), preferably from about 0.01 psig (0.07 kPag) to about 500 psig (3500 kPag), and most preferably from about 0.01 psig (0.07 kPag) to about 100 psig (700  
10 kPag).

The pressure in pressurizing step (b) and the pressurizing mixing step (c) usually ranges from about 1000 psig (7000 kPag) to about 10,000 psig (70,000  
15 kPag), preferably about 1000 psig (7000 kPag) to about 5000 psig (35,000 kPag), and more preferably from about 1500 psig (10,000 kPag) to about 3000 psig (21,000 kPag).

20 The conditions for cooling, depressurizing and foaming can be those commonly used in the art such as disclosed in Corbett et al., U.S. Patent No. 3,770,668 and McCurdy et al., U.S. Patent No. 2,669,751.

25 Corbett et al. discloses styrenic polymer foams and methods and apparatus for extrusion thereof. McCurdy et al. discloses an improved process for the preparation of thermoplastic foam. One feature of the improvement is a method for mixing and cooling of the  
30 resin gel in a vessel downstream from an extruder.

35 One embodiment of an apparatus suitable for carrying out the process of the invention is shown in Fig. 1. Such apparatus can be employed for continuous production of thermoplastic resin foam compositions. Included is a melting-mixing means 10 for melting at

-13-

1 ast one thermoplastic resin to a liquid state and  
mixing the resin to form a resin melt. It is essential  
that the melting-mixing means have moving mixing  
elements that are adapted by spacing between the moving  
5 mixing elements and interaction thereof to accomplish  
substantial mixing of the resin substantially without  
sufficient shear to cause a localized temperature rise  
at which substantial depredation of the resin occurs.

10 In a preferred embodiment for making resin foam  
compositions the melting-mixing means 10 is adapted to  
accomplish substantial mixing without sufficient shear  
to cause a localized temperature rise in the temperature  
of the resin melt to greater than about 40°C to about  
15 150°C above the Tg or Tm of the resin, but preferably  
without raising the temperature from about 40°C to about  
100°C above the Tg or Tm and more preferably to no more  
than about 50°C to 90°C above the Tg or Tm. The moving  
20 mixing elements in melting-mixing means 10 are  
preferably twin spaced apart screws each having spiral  
flights thereabout.

Suitably, the mixing screws are spaced about  
25 0.125 inches (in)(0.32 centimeter(cm)) to about 0.25 in  
(0.65 cm) apart to avoid unwanted shear action. The  
mixing screws are mounted within a chamber or vessel  
having heating and cooling elements externally attached  
to the chamber wall. The mixing chamber is also  
30 provided with an inlet for continuous feed of  
thermoplastic resin, usually in particulate or  
pelletized form. The chamber at the discharge end of  
the chamber is provided with an outlet 11 for discharge  
of resin melt into a conduit leading to the inlet of a  
35 suitable pump means 12.

- 14 -

The means for causing resin melt to discharge from the outlet of the melting-mixing means may be gravity flow, e.g. by vertical disposition of the mixer, or the action of the moving mixing means but preferably 5 is a pre-pressurizing means adjacent the outlet adapted to discharge resin melt at a pressure up to about 980 psig (6800 kPag). Preferably, the pre-pressurizing means is a modified distal section of the moving mixing elements of the melting-mixing means adapted to 10 discharge resin melt at a pressure preferably in the range of about 0.01 psig (0.07 kPag) to about 100 psig (700 kPag). The pressurized resin melt exiting the pump 12 via an outlet is led through a conduit to the inlet 15 of pressurized mixing means 13.

A preferred melting-mixing means is a modification of a compounder or a continuous mixer as disclosed in Ahlefeld, Jr. et al., U.S. Patent No. 20 3,154,808.

The pump means 12 is preferably a gear pump and is used for pressurizing the resin melt to a pressure in the range of about 1000 psig (7000 kPag) to about 10,000 25 psig (70,000 kPag), preferably from about 1500 psig (10,000 kPag) to about 3000 psig (21,000 kPag). The pump means 12 has an outlet and means for metering resin melt through the outlet. The pump means used must be capable of handling a rather viscous resin melt and 30 function without causing substantial temperature rise of the melt.

The pressurized mixing means 13 is used for dispersing blowing agent material into the resin melt 35 within a pressurized zone. The pressurized mixing means may be most any mixing vessel or chamber equipped with

-15-

mixing elements and adapted to receive and mix resin melt and blowing agents under a preselected pressure in the range of about 1,000 psig (7000 kPag) to about 10,000 psig (70,000 kPag), the pressure being sufficient  
5 to maintain the blowing agents in a substantially miscible form in the melt. While the resin melt is fed continuously into the pressurized mixing means through an inlet 15 under the preselected pressure the blowing agents are continuously injected into the mixing chamber  
10 through another inlet 14. The mixing elements may for example be pins projecting in opposed directions from a cylindrical rotor and a surrounding stator, or the mixing may be accomplished with a cavity-transfer mixer  
15 with an overlapping array of cup shaped concave recesses in each of the rotor and the stator and a relatively small annular spacing. A combination of mixing means may be employed to disperse blowing agent material in the resin melt.

20 Preferably, the pressurized mixing means 13 of Fig. 1 is an in-line kinetic mixer, an example of which is disclosed by McCurdy et al., U.S. Patent No. 2,669,751. In another preferred embodiment the  
25 pressurized mixing means 13 comprises a cavity-transfer mixer. Cavity-transfer mixers are disclosed in Gale, U.S. Patent No. 4,419,014.

It is desirable to get substantially  
30 homogeneous dispersion of the blowing agent in the resin melt to form a resin gel while at the same time not generating excessive local heating because of mechanical work input.

35 It is essential to maintain a pre-selected pressure in the mixing chamber and keep the blowing

- 16 -

agent from forming a foam until the gel subsequently is released through a foam forming orifice.

The resin gel is discharged under pressure from  
5 the pressurized mixing means 13 through outlet 16 and  
through a conduit to the inlet of the cooling-  
depressurizing means 19. The cooled gel exits the  
cooling-pressurizing means at an outlet and enters the  
foam-forming die orifice means 20. After the gel leaves  
10 the die orifice, the gel is formed into a foam or  
foamable composition. The particular shape and  
properties of the resin foam composition are further  
controlled after the gel exits the die orifice using  
temperature and pressure modifying means.  
15

The cooling-depressurizing means and the foam-  
forming die orifice means may take the form of most any  
of the equipment known in the art for the purpose of  
making foam. Entirely suitable and preferred equipment  
20 is described in Corbett, U.S. Patent No. 3,770,668.

If desired, in order to assure more uniform  
cell size in the foam product it may be desirable to  
25 pass the cooled resin gel, while still under pressure,  
through a static mixer 40, or series of static mixers  
before releasing the pressurized gel to a reduced  
pressure, e.g. ambient atmospheric pressure, through a  
typical foam-forming die orifice. The foam forming at  
30 the orifice will be directed into making foam sheets,  
foam boards, foam particles and other typically extruded  
foam compositions using the appropriate post-die forming  
means such as a mandrel, forming shoes, forming plates  
and other typical post-die orifice means as well

35

understood in th art. Foamabl compositions can also be made.

In order to monitor the temperature and  
5 pressure of the resin melt and resin gel throughout the system a metering sensor means 21 connected to the output of the melting-mixing means 10 is provided; a metering sensor means 22 connected to the conduit between the pump means 12 and pressurized mixing means 10 13 is provided; a metering sensor means 23 connected to the conduit between the pressurized mixing means 13 and the cooling-depressurizing means 19 is provided; and a metering sensor means 24 connected to the conduit between the cooling-depressurizing means 19 and the 15 foam-forming die orifice means 20 is provided.

Another embodiment of the apparatus production line of the invention is shown in Fig. 2, which is similar to Fig. 1 with the exception of a modification 20 of the pressurized mixing means 13 as illustrated. A melting-mixing means 30 corresponds to the melting-mixing means 10 of Fig. 1. A pump means 32 corresponds to the pump means 12 of Fig. 1. The essential difference between the figures is that the pressurized mixing means 13 of Fig. 1 is replaced by a pressurized mixing means 33 and a second pressurized mixing means 37. Pressurized mixing means 33 comprises an in-line kinetic device such as a spline mixer and pressurized 25 mixing means 37 comprises a cavity-transfer mixer. This arrangement of mixing devices is preferable when processing resin melts or gels at or near the Tg or Tm 30 of the resin. In a further embodiment it may be preferable for pressurized mixing means 33 to comprise a 35

-18-

cavity-transf r mixer and pressurized mixing means 37 to comprise a spline mixer.

5           Example 1 - Production of High Bromine Containing Polystyrene Foam

Equipment

10           Fig. 1 illustrates schematically apparatus used in a pilot line to produce polystyrene foam compositions containing high levels of bromine. The melting-mixing means 10 is a Farrel 2CM Continuous Mixer™ brand mixer (Pomini Farrel Corp., Castellanza, Italy). The pump means 12 is a Luwa Vacorex Gear Pump™ brand gear pump (Maag-Luwa Corp., Zurich, Switzerland). The pressurized mixing means 13 is an in-line kinetic mixing device as disclosed by McCurdy et al., U.S. Patent No. 2,669,751. The cooling-depressurizing means 19, and foam-forming die orifice means 20 of Fig. 1 are as disclosed in 15 Corbett et al., U.S. Patent No. 3,770,668. The optional static mixer mixing means 40 of Fig. 1, directly preceding the foam-forming die orifice is of conventional design and is optionally included to improve uniformity of foam composition.

25           The apparatus is clad substantially throughout by an insulating jacket and the temperature and pressure readings are monitored with metering and sensor means 21, 22, 23 and 24, Fig. 1. The temperature of the 30 mixing chamber and the the mixing chamber orifice is controlled through the use of electric heaters and cooling devices and the temperatures of the remaining portions of the apparatus are independently controlled 35 through the use of jacket insulation standard in the industry.

-19-

Method

Using the equipment described above a series of polystyrene foam samples are produced containing different amounts of hexabromocyclododecane (HBCD).

This fire retardant is added to the thermoplastic resin melt in proportions in the range of 1.4 weight percent to 3.3 weight percent.

Table I shows various formulations of the thermoplastic resin composition processed at a production rate of 200 lbs (90 kg) per hour. Table III shows the actual amount of fire retardant in each sample formulation.

15

TABLE I  
Foam Composition and Feed Rate

	<u>MATERIAL</u>	<u>FEED RATE IN LB/HR</u>	<u>FEED RATE IN KG/HR</u>
20	Polystyrene (weight average MW of about 200,000)	200	91
	HBCD	Varied as indicated*	
	Magnesium Oxide	0.15	0.07
25	Talc	0.60	0.27
	Low Density Polyethylene (LDPE)	0.26	0.12
	Tetrasodiumpyrophosphate (TSPP)	0.30	0.14
	Ethyl Chloride	7.6	3.4
30	Dichlorodifluoromethane (CFC-12)	15.2	6.9
	Carbon Dioxide	2.2	1.0

\*1.4 weight percent to 3.3 weight percent of the resin as represented in Table III.

35

-20-

Table II shows temperatures, pressures and production rates at various points in the system including the Farrel Continuous Mixer (FCM), the gear pump, and the in-line kinetic mixer (IKM).

TABLE II  
PROCESS CONDITIONS

	<u>Process Temperatures deg C</u>					
	<u>Sample</u>					
	1	2	3	4	5	6
Out FCM	162.8	162.3	163.1	162.6	162.7	162.3
Out Gear Pump	164.1	163.1	164.5	163.1	164.2	163.2
Out IKM	181.8	181.5	181.8	180.9	181.6	181.1
1 Die	125.0	125.1	125.0	125.0	125.1	125.0
<u>Process Pressures psig (kPa)</u>						
Out Gear Pump	2260 (15580)	2310 (15930)	2210 (15210)	2220 (15307)	2200 (15170)	2200 (15170)
Out IKM	1780 (12270)	1700 (11720)	1730 (11930)	1740 (12000)	1720 (11859)	1710 (11790)
<u>Board Speed ft/min (m/min)</u>						
	56.4 (17.2)	57.2 (17.4)	56.5 (17.2)	57.0 17.4	53.2 (16.2)	55.7 (17.0)

The maximum processing resin gel temperature of any sample is under 185°C. The density of all foam product samples is approximately 2.1 lb/ft<sup>3</sup> (33.6 kg/m<sup>3</sup>). The cell size of all foam product samples is between 0.3 and 0.4 millimeters.

Table III shows the densities and cell sizes of the samples as a measure of quality of foam product. The amount of fire retardant is varied while density and cell size remain substantially uniform and constant as demonstrated using standard ASTM testing methods.

-21-

Visual examination of various portions of the foam shows no instances of any evidence of thermal degradation of either the resin or the fire retardant.

TABLE III

5

Foam Properties as a Function of Bromine Content

	<u>Sample</u>	<u>Weight Percent HBCD in Resin</u>	<u>Weight Percent Bromine in Resin</u>	<u>Density lb/ft<sup>3</sup> (kg/m<sup>3</sup>)</u>	<u>Cell Size (mm)</u>
10	1	1.4	.90	2.10 (33.6)	.36
	2	1.8	1.16	2.10 (33.6)	.37
	3	2.2	1.41	2.11 (33.8)	.34
15	4	2.5	1.60	2.10 (33.6)	.35
	5	2.9	1.88	2.08 (33.3)	.35
	6	3.3	2.05	2.11 (33.8)	.35

Example 2 - Production of Rubber-Modified Polystyrene Foam With Desirable Levels of Fire Retardant

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A pilot plant line corresponding to the apparatus of Example 1 is employed to produce rubber-modified polystyrene (RMPS) foam composition samples with desirably high levels of preferred fire retardant.

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The processing is initiated with a virgin feed of polystyrene and subsequently the polymeric feed is switched to a rubber-modified polystyrene resin wherein the polystyrene is of weight average MW in the range of 200,000 +/- 1,000 and contains dispersed polymeric butadiene particles in an amount of about 8.5 weight

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-22-

percent of the resin weight. The process is controlled to give a foam-forming die orifice pressure of 700 ± 100 psig (4800 ± 700 kls). The temperature in mixing chamber and at the outlet of the Farrel Continuous Mixer (FCM), the melting-mixing means 10, is maintained at about 175°C. The gear pump speed is adjusted to give output rates of about 200 lbs/hr (90 kg/hr).

The resin formulations of the seven foam samples are given in Table IV. The amount of two of the blowing agents, ethyl chloride and carbon dioxide are varied between the resin formulations as carbon dioxide is used to enhance cell nucleation. The weight percent units are based on the weight of RMPS.

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-23-

TABLE IV  
FORMULATION DATA

	<u>Resin Composition</u>	<u>Units</u>	<u>Samples</u>						
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
5	RMPS	lb/hr	200	200	200	200	200	200	200
		kg/hr	90	90	90	90	90	90	90
10	HBCD	weight percent	1.6	1.6	1.6	1.6	1.6	1.6	1.6
15	Talc - 15% Conc. in polystyrene	weight percent	0.4	0.4	0.4	0.4	0.4	0.4	0.4
20	Magnesium Oxide	weight percent	0.1	0.1	0.1	0.1	0.1	0.1	0.1
25	Difluorodi- chloromethane	weight percent	6.1	6.1	6.1	6.1	6.1	6.1	6.1
30	Ethyl Chloride	weight percent	4.0	2.6	2.6	2.6	2.6	2.6	2.6
35	Carbon Dioxide	weight percent	1.1	2.0	2.9	2.4	2.9	2.4	2.9

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The process variables used to produce the seven foam samples are listed in Table V.

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-24-

TABLE V  
PROCESS VARIABLES

	<u>Units</u>	<u>Samples</u>						
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Feed Rate of RMPS	lb/hr kg/hr	200 90	200 90	200 90	200 90	200 90	200 90	200 90
Sample Width	inch mm	5.8 147	4.6 117	4.3 109	4.6 117	4.6 117	3.7 94	4.1 104
Sample Thickness	inch mm	1.0 25	0.9 23	0.9 23	0.9 23	0.8 20	0.8 20	0.9 23
Board Speed	ft/min m/min	-- --	-- --	79 24	67 20	75 23	95 29	-- --
<u>System Temperatures</u>								
Out FCM	°C	169	170	171	170	170	170	170
Out Gear Pump	°C	169	169	171	171	170	171	170
Out IKM	°C	191	190	190	191	189	190	189
<u>System Pressures</u>								
FCM Outlet	psig kPag	<10 <69	<10 <69	<10 <69	<10 <69	<10 <69	<10 <69	<10 <69
Gear Pump Outlet	psig kPag	2720 18,750	2510 17,310	2530 17,440	2750 18,960	2680 18,480	2550 17,580	----

The density and cell size for the resultant foam samples are shown in Table VI. The density ranges from about 1.4 lb/ft<sup>3</sup> (22.4 kg/m<sup>3</sup>) to about 2.3 lb/ft<sup>3</sup> (36.8 kg/m<sup>3</sup>) and the cell size ranges from about 0.5 mm to 30 about 1.7 mm in diameter. These results indicate that blowing agent efficiency is maintained. No evidence of thermal degradation of resin or fire retardant is found in any of the samples upon visual examination.

-25-

TABLE VIFOAM PROPERTY DATA

	<u>Sample</u>	<u>Units</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
5	Density	lb/ft <sup>3</sup>	2.30	1.74	1.63	1.80	1.81	1.66	1.38
	ASTM Test	kg/m <sup>3</sup>	36.8	27.9	26.1	28.8	29.0	26.6	22.1
	D-1622								
	Cell Size								
	ASTM Test	mm	1.74	0.79	0.57	0.59	0.58	0.63	0.50
	D-3176								

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Example 3 - Apparatus for Production of Polystyrene Foam Under Low Temperature Conditions

Utilizing the apparatus of Fig. 2, a thermoplastic polystyrene resin foam composition is produced utilizing as the melting-mixing means 30 a Farrel FCM Continuous Mixer™ brand mixer, model 6UM (Farrel Company, Ansonia, CT); as the pump means 31, a Luwa Vacorex Gear Pump™ brand gear pump (Maag-Luwa Corp., Zurich, Switzerland); as the pressurized mixers 33 and 37 in tandem, an in-line kinetic mixer as disclosed in McCurdy et al., U.S. Patent No. 2,669,751 and a cavity-transfer mixer; a conventional cooling-depressurizing means 39 such as that disclosed in Corbett et al., and a conventional foam-forming die orifice means 41.

Resin and additives listed in Table IX are fed into the mixing chamber of the melting-mixing means 30. The blowing agents, introduced into the first pressurized mixing means 33 at point 36 are about 30 7 percent by weight of difluorodichloromethane, about 1.5 percent by weight CO<sub>2</sub> and about 3 percent by weight ethyl chloride, based on the total resin gel 35 composition.

-26-

The preferred operating temperature range is about 140°C to about 195°C. The resin melt temperature is about 140°C to about 185°C. The resin gel temperature is about 150°C to about 190°C. The gear pump input pressure 5 is about 0.01 psig (0.07 kPag) to about 50 psig (350 kPag). The gear pump output pressure is about 1500 psig (10,300 kPag) to about 2500 psig (17,200 kPag).

No evidence of thermal degradation is found in the 10 product.

TABLE IX  
RESIN FORMULATION

	<u>Ingredient</u>	<u>Weight %</u>
15	Polystyrene (about 200,000 MW)	about 84.045% by weight
	HBCD	3.0%
	Magnesium Oxide	0.015%
	TSPP	0.15%
20	LDPE	0.1%
	Barium or Calcium Stearate	0.15%
	Talc	1.0%

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CLAIMS

1. A continuous method of preparation of a thermoplastic resin foam or foamable composition comprising sequentially the steps of:

- (a) melting and mixing at least one thermoplastic resin to form a resin melt, the mixing process being carried out without applying shear forces of sufficient thermal energy to cause a localized rise in temperature of the resin melt to a temperature at which substantial degradation of the resin occurs;
- (b) pressurizing to and maintaining the resin melt at a pressure sufficient to permit introduction of one or more blowing agents into the resin melt at a temperature below the temperature at which substantial degradation of the resin melt occurs;
- (c) introducing and dispersing the one or more blowing agents substantially throughout the resin melt to form a resin gel at a temperature above the glass transition temperature or the melt temperature of the thermoplastic resin and below a temperature at which substantial degradation of the resin gel occurs; and
- (d) cooling and depressurizing the resin gel, the depressurizing being carried out at a sufficiently cool temperature for formation of a foam or foamable

composition with structural integrity, and the cooling and depressurizing being carried out substantially at the same time;

(e) either foaming and forming the resin gel 5 to form a solid foam composition or foaming the resin gel to form a solid foamable composition;

the recited steps being carried out continuously in a series of stages with the temperature 10 of the resin melt and gel being maintained substantially independently of the flow rate of the resin melt and gel advancing through and between the stages.

2. A method as claimed in Claim 1, wherein 15 the resin is selected from polystyrene, rubber-modified polystyrene, and rubber-modified polyethylene.

3. A method as claimed in Claim 2, wherein the resin is selected from rubber modified polystyrene 20 or polyethylene containing 3 to 30 weight percent (based on total resin weight) dispersed polymeric butadiene particles.

4. A method as claimed in any one of the 25 preceding claims, wherein the resin contains 0.01 to 5 weight percent (based on total resin weight) of a fire-retardant.

5. A method as claimed in Claim 4 wherein the 30 fire retardant is selected from hexabromocyclododecane, pentabromomonochlorocyclohexane and tetrabromobisphenol A.

6. A method as claimed in any one of the preceding claims, wherein the resin melt is pr -

pressurized prior to step (b) to a pressure range from 0.07 kPag (0.01 psig) to 7,000 kPag (980 psig).

7. A method as claimed in any one of the preceding claims, wherein the pressure of step (b) is  
5 from 7,000 kPa (1000 psig) to 70,000 kPa (10,000 psig).

8. An apparatus for continuous production of thermoplastic resin foam or foamable compositions by a method as claimed in Claim 1, said apparatus comprising:

10 (a) melting-mixing means for melting and mixing a resin to form a resin melt, the melting-mixing means having moving mixing elements and being adapted by the spacing between the moving mixing elements and  
15 interaction thereof to accomplish substantial mixing of the resin melt essentially without shear forces of sufficient thermal energy to cause a localized temperature rise in the temperature of the resin melt to greater than 150°C above the glass transition  
20 temperature or the melt temperature of the resin, the melting-mixing means having an inlet for the resin and an outlet for the resin melt, and means for causing the resin melt to discharge from the outlet;

25 (b) pump means for pressurizing the resin melt to a pressure in the range of 7,000 kPa (1000 psig) to 70,000 kPa (10,000 psig), the pump means having an inlet and an outlet and means for metering the resin melt through the outlet;

30 (c) pressurized mixing means for dispersing blowing agents in the resin melt within a pressurized zone to form a resin gel, the pressurized mixing means being provided with an inlet for introducing the blowing

-30-

agents, an inlet for the resin melt, and an outlet for discharging the resin gel under pressure;

(d) cooling-depressurizing means for concurrently cooling and depressurizing the resin gel to 5 a temperature and pressure sufficient for discharging the resin gel through a foam-forming die orifice means; the cooling-depressurizing means having an inlet for receiving the resin gel under pressure and an outlet for the cooled gel; and

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(e) conduit means providing fluid communication respectively and sequentially between the outlet of the melting-mixing means and the inlet of the pump means, between the outlet of the pump means and the 15 inlet of the pressurized mixing means, between the outlet of the pressurized mixing means and the inlet of the cooling-depressurizing means and between the outlet of the cooling-depressurizing means and the foam-forming die orifice means.

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9. An apparatus as claimed in Claim 8, wherein the moving mixing elements of the melting-mixing means are twin spaced-apart screws having spiral flights thereabout.

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10. An apparatus as claimed in Claim 8 or Claim 9, wherein the pre-pressurizing means comprises a modified distal section of the moving mixing elements of 30 the melting-mixing means.

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11. An apparatus as claimed in any one of Claims 8 to 10, wherein the pump means comprises a gear pump.

-31-

12. A thermoplastic foam composition comprising a resin selected from the group consisting of: rubber-modified polystyrene resin and rubber-modified polyethylene resin; and 0.01 weight percent to 5 weight percent by resin weight of a fire retardant wherein the resin has 3 weight percent to 30 weight percent rubber based on total resin weight.

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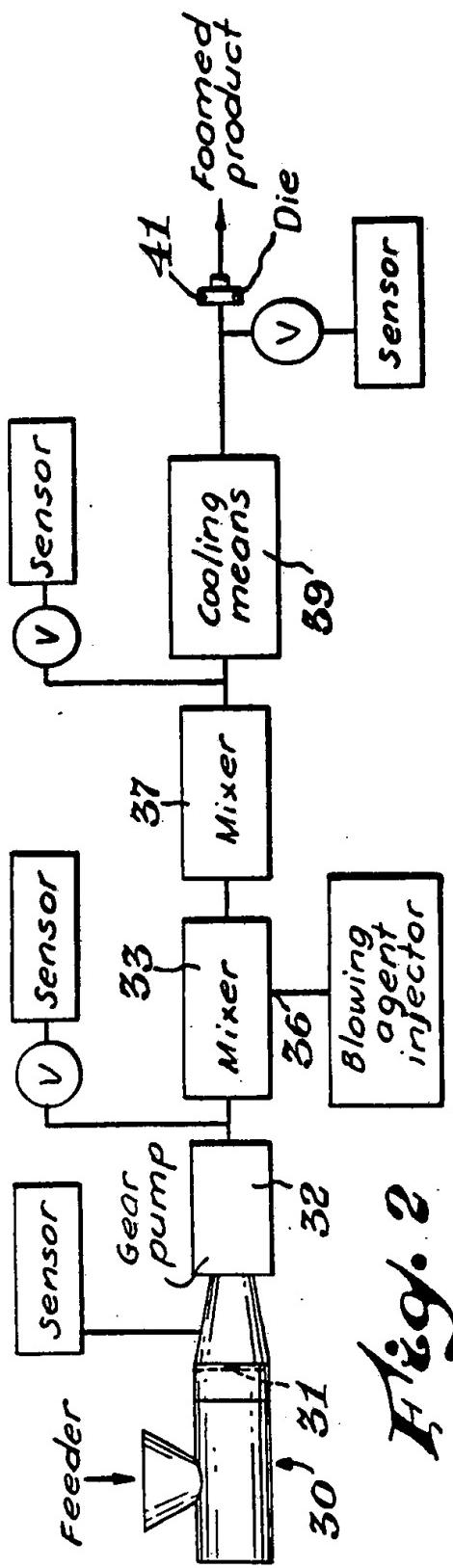
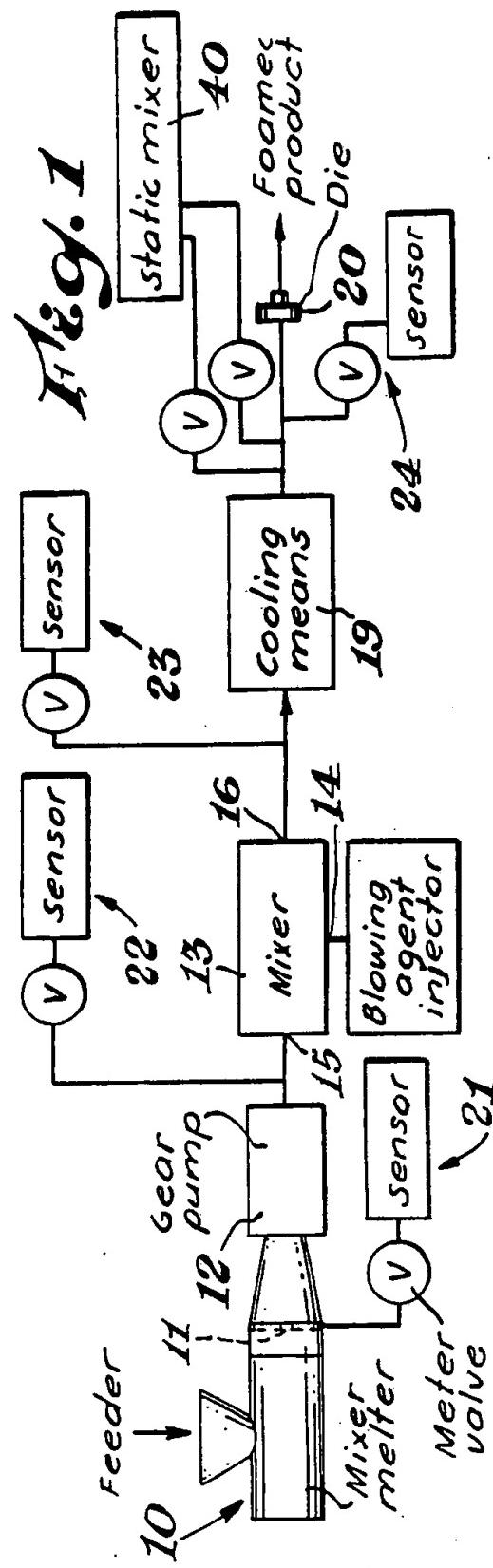
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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/05865

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5) B29B 7/30, 7/32, 7/46; C08J 9/12, 9/14, 9/30  
US CL 264/53; 425/4C, 366, 378.1, 817C; 521/79, 81, 139, 140

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System	Classification Symbols
U.S.	264/53; 425/4C, 366, 378.1, 817C; 521/79, 81, 139, 140

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4,436,679 (WINSTEAD) 13 March 1984 See entire document	1-11
X	US, A. 3,830,901 (WINSTEAD) 20 August 1974 See entire document	1-11
Y	US,A, 4,615,664 (KOLOSSOW) 07 October 1986 See entire document	1-11
Y	US, A, 4,469,651 (HAHN ET AL.) 04 September 1984 See entire document	1-11
Y	US,A, 4,454,087 (HAYASHI ET AL.) 12 June 1984 See entire document	1-11
Y	US, A, 4,560,334 (RUTLEDGE) 24 December 1985 See entire document	1-11
Y	US, A, 4,299,792 (NUNN) 10 November 1981 See entire document	1-11
A	US, A, 2,515,250 (MCINTIRE) 18 July 1950	1-11

\* Special categories of cited documents: <sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

14 MARCH 1990

Date of Mailing of this International Search Report

02 APR 1990

International Searching Authority

ISA/US

Signature of Authorized Officer:

MORTON FOELAK

*Morton Foelak*  
HO NGUYEN

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 2,023,204 (MUNTERS ET AL.) 03 December 1935 See entire document	1-11
X	US, A, 4,370,378 (ZABROCKI ET AL.) 25 January 1983 See entire document	12
A	US, A, 3,959,197 (SALYER ET AL.) 25 May 1976 See entire document	1-11
X	US, A, 4,198,486 (MYLICH ET AL.) 15 April 1980 See entire document	12
Y	US, A, 4,207,402 (SPEENKLE, JR.) 10 June 1980 See entire document	12

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers \_\_\_\_\_ because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2.  Claim numbers \_\_\_\_\_ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

3.  Claim numbers \_\_\_\_\_ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

(Telephone practice , see attachment)

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

**III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)**

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	US, A, 4,323,655 (DIGIULIO ET AL.) 06 April 1982 See entire document	12
X	US, A, 4,439,547 (DIGIULIO ET AL.) 27 March 1984 See entire document	12
P,X	US, A, 4,851,453 (WHITE ET AL.) 25 July 1989 See entire document	12
X	US, A, 4,762,861 (BOHEN ET AL.) 09 August 1988 See entire document	12
P,X	US, A, 4,812,484 (ENDO ET AL.) 14 March 1989 See entire document	12
P,X	US, A, 4,849,473 (CIGNA ET AL.) 18 July 1989 See entire document	12
X	US, A, 3,669,923 (HINTZ) 13 June 1972 See entire document	12
X	US, A, 4,246,211 (KUHNEL) 20 January 1981 See entire document	12

OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

- I. Claims 1-11 are drawn to a continuous method of making a resin foam by extrusion and an apparatus for carrying out said process and would be classified in class 264 subclass 53 and class 423 subclass 4C.
- II. Claim 12 is drawn to a rubber modified resin foam containing a flame retardant and is classified in class 521 subclass 139.

These distinct and independant inventions lack unity of invention and fail to comply with the combinations permitted by PCT Rule 13.2 (i) - (iii).

The process and apparatus claims are not limited to "an" independent claim "specifically adopted for the manufacture of the product".

The product could be produced by a materially different process and apparatus such as by an injection molding process and apparatus.